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A Comparative Study of Two Methods of Vaporizing a Paraffin-Base Petroleum

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A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

BY
A. J. GOOD
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EASTON, PA.:
MACK PRINTING COMPANY
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[Reprinted from Industrial and Engineering Chemistry, Vol. 19, No. 4, p. 453. April, 1927.]

The Vaporization of Petroleum[1]

A Comparative Study of Two Methods of Vaporizing a Paraffin-Base Petroleum

By E. H. Leslie and A. J. Good

University of Michigan, Ann Arbor, Mich., and E. B. Badger & Sons Co., Boston, Mass.

Methods of vaporization are briefly discussed and classified.

A paraffin-base petroleum has been vaporized by equilibrium single flashing and equilibrium successive flashing at each of a series of temperatures, and the distillates and residuums so obtained analyzed by a method that gives true boiling point curves.

Single flashing has been found superior to successive flashing as regards yield of distillate, exhaustion of residuum, composition of vapor, and heat requirement. The proportion of a single-flash distillate boiling below the flash temperature averages 82.3 per cent and of a successive flash distillate 80.65 per cent. The proportion of a single-flash residuum boiling below the flash temperature averages 11.6 per cent, and of a successive flash residuum 16.4 per cent.

The A. S. T. M. end point of the standard column flask residue from a single-flash distillate averages 165° F. above the flash temperature. This is 10° to 15° F. above the A. S. T. M. end point of the distillate. The A. S. T. M. end point of the standard-column flask residue from a successive flash distillate averages 150° F. above the flash temperature.

The distillation curves of flash vaporization products are related to each other after the manner of a geometric progression.

The results of this investigation are discussed briefly with regard to their application in petroleum distillation practice.

THE distillation of petroleum should properly be considered as comprising two steps—the formation of the vapor and the fractionation of the vapor. The petroleum technologist recently has devoted considerable attention to methods of fractionation, with the results that they have been greatly improved. In modern plants rerunning has been eliminated and products of desired characteristics have been obtained by applying the principles of countercurrent extraction—that is, efficient distillation with columns in various arrangements, as distinguished from fractionation by partial condensation. The tendency, however, has been to add column equipment to existent stills or other vaporization equipment, a procedure that may be justified in many instances by expediency and costs but which may sometimes overlook vital factors in the formation of the vapor.

The subject of vapor formation from petroleum is too broad to be covered in detail with regard to all its aspects in a single paper, nor is this possible in view of the limitations of our present knowledge. The purpose of the present discussion is to direct attention to the importance of the manner of vapor formation and to present the results of an investigation covering the equilibrium single-flash and equilibrium successive-flash vaporization of a paraffin-base petroleum containing approximately 50 per cent of gasoline.

Type Methods of Vaporization

Methods of vaporization may be classified as (1) differential, (2) differential incremental, and (3) incremental.

Differential vaporization is a process in which successive differential quantities of heat are supplied, with the result that corresponding differential weights of vapor are formed, each of which is removed as soon as formed. This ideal process is never exactly achieved in practice, but batch or simple distillation is a close approach. If the liquid vaporized is petroleum, or other complex solution, it is apparent that each small weight of vapor is different in composition from any other and that the composition of the vapor exiting from the vaporization system varies continuously from the beginning to the end of the operation.

Differential incremental vaporization is a process in which heat is supplied to a flowing stream of the liquid in such manner that successive differential weights of vapor are formed and that these differential quantities of vapor are caused to join and comprise a quantity of vapor that is a sizable proportion, or even the whole, of the vapor formed. For example, consider a battery of stills so arranged that the liquid to be vaporized flows from still to still. In any particular still the liquid flows from one end to the other. Heat is continuously supplied to the bottom of the still. Each small quantity of heat transferred results in the formation of a small weight of vapor. The liquid from which this vapor was formed flows along and is further heated and vaporized in a like manner. All the small quantities of vapor so formed join to form the vapor that exits from the still. The exiting vapor constitutes a considerable part, or increment, of the vapor formed in the entire battery. If the "battery" is a single still, fed and overflowed continuously, the vapor is removed as a single increment.

Incremental vaporization may be defined as a process in which the liquid is heated and then flashed in such manner as to produce an equilibrium vapor and residuum. Pressure sufficient to prevent vaporization may be held on the liquid, in which event the formation of the vapor takes place upon release of the pressure. The liquid and vapor should be in intimate contact during the time of vapor formation so that equilibrium will be established. Another procedure productive of the same result is one in which vapor formation is progressive but also in which all the liquid and all the vapor are in intimate contact until separated after all the heat has been added.

If the process of incremental vaporization is such that all of the vapor is removed in one step, the procedure may be designated as "single-flash" vaporization. If several increments of vapor are removed—that is, if the process is a stepwise one involving the formation of several equilibrium vapors and liquids—it may be designated as "successive-flash" vaporization. Pipe-still practice affords examples of both the single-flash and the successive-flash processes. However, all pipe-stills and vaporizers are not so designed and operated as to produce equilibrium vapors and residuum.

The present investigation was confined to a comparative study of single-flash and successive-flash vaporization. If a given part of a crude petroleum is to be vaporized,

[1] Received December 9, 1926.

is it better to form the vapor in one step or in several steps? What are the compositions of the resulting vapor and residuum when they are formed in each of these two ways? What are the heat requirements in the two cases? The answers to these and other similar questions were desired.

The refinery engineer is interested in securing from the crude, a maximum yield of distillate of gasoline boiling

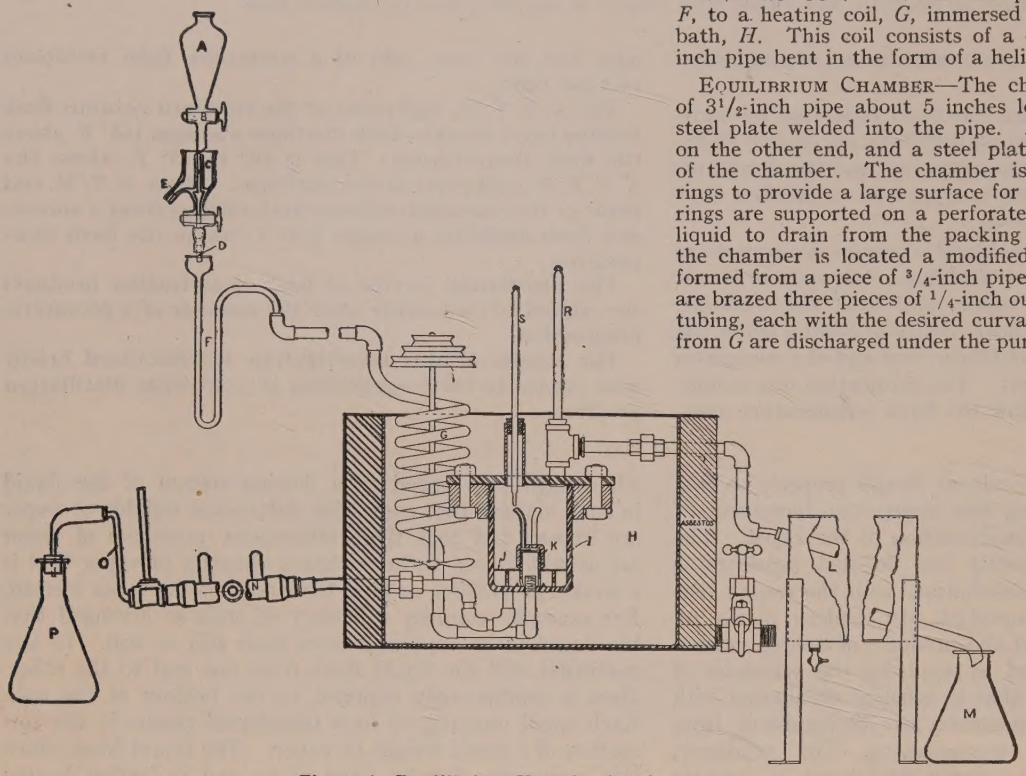

Figure 1—Equilibrium Vaporization Apparatus

range. This implies complete exhaustion of the gasoline from the residuum. Furthermore, if all the gasoline is vaporized, what is the nature of the balance of the vapor? That is, what proportion of higher boiling substances that must be removed by fractionation is contained in the vapor?

Experimental Procedure

In order to study incremental vaporization it was necessary to provide laboratory equipment that would operate continuously to produce an equilibrium vapor and residuum. The attainment of equilibrium is influenced by three main factors—extent of the vapor-liquid interface, intimacy of contact of vapor and liquid, and time.

To meet these conditions, and to permit practical and successful operation, the apparatus shown in Figure 1 was built. It consists essentially of six parts: (1) feed device designed to supply material to the heating coil at a definite, constant rate; (2) a coil to heat and partially vaporize the liquid previous to its admission to the equilibrium chamber; (3) an equilibrium chamber in which the vapor produced is contacted with a liquid containing the same components; (4) a condenser to recover the vapor liberated in the equilibrium chamber; (5) a residuum cooler; and (6) a constant-temperature bath.

Constant-Feed Device—The solution to be vaporized is placed in the 500-cc. dropping funnel, *A*, in the bottom of which is a small amount of absorbent cotton to remove any suspended foreign material such as the sand that may be present in crude petroleum. Controlled by means of the stopcock *B*, the solution is allowed to drop into a constant-head device, *C*, at a known rate slightly greater than the desired feed rate. An orifice, *D*, made by constricting a short length of capillary tubing, controls the rate of feed to the equilibrium chamber. This feed rate can be altered at will by replacing the orifice with one of a different size. The material from *B*, in excess of that delivered through the orifice *D*, is wasted through the outlet *E*. With a definite orifice and a constant liquid head, the rate of feed is constant.

Heating Coil—The solution passes through a liquid seal, *F*, to a heating coil, *G*, immersed in the constant-temperature bath, *H*. This coil consists of a 4-foot piece of standard $^1/_4$-inch pipe bent in the form of a helix of 3-inch diameter.

Equilibrium Chamber—The chamber *I* consists of a piece of $3^1/_2$-inch pipe about 5 inches long, closed at one end by a steel plate welded into the pipe. A cast-iron flange is screwed on the other end, and a steel plate bolted to it forms the top of the chamber. The chamber is filled with $^1/_4$-inch Lessing rings to provide a large surface for vapor-liquid contact. These rings are supported on a perforated plate, *J*, which allows the liquid to drain from the packing material. In the center of the chamber is located a modified Cottrell pumping tube, *K*, formed from a piece of $^3/_4$-inch pipe and a standard cap to which are brazed three pieces of $^1/_4$-inch outside diameter seamless steel tubing, each with the desired curvature. The liquid and vapor from *G* are discharged under the pumping tube *K*. A mixture of vapor and liquid is sprayed onto the packing, where the vapor separates from the liquid, rises through an inch of packing to remove entrainment, and passes into a delivery tube that terminates in the condenser, *L*. The liquid drains through *J* into the pool in the bottom of the chamber. The liquid in this pool is kept in constant circulation by the action of the pumping tube. The depth of the pool of residual liquid is controlled by raising or lowering the adjustable tube, *O*, and all excess material flows by gravity through the cooler *N* to the receiver *P*. Two vents on the residuum draw-off prevent the liquid pool in the chamber from being siphoned into the receiver.

Condenser—This is a copper-and-brass unit from a standard A. S. T. M. distillation outfit and is kept at the temperature of melting ice. The condensate passes into a closed suction flask imbedded in cracked ice.

Residuum Cooler—The cooler consists of two concentric iron pipes with water flowing through the annular space as a cooling medium. The liquid is collected in a closed suction flask kept at any desired temperature by a suitable bath.

Constant-Temperature Bath—The bath *H* is contained in a steel box, heavily insulated, with a liquid capacity of about 9 gallons. The liquid level is kept high enough completely to cover the equilibrium chamber and vapor outlet tube. Under this condition no condensation can occur; the vapor passing to the condenser must be identical with that formed in the equilibrium chamber. For all temperatures up to 400° F. the bath liquid was a heavy midcontinent petroleum residuum. The heat was supplied by three nichrome-wire heating coils and was regulated by a slide-wire resistance. The temperature could be controlled readily to within 0.5° F., which was sufficiently accurate. For temperatures above 400° F. the liquid in the bath was a fused equimolar mixture of sodium and potassium nitrates. When using the nitrate bath the heat was supplied by gas burners, the temperature control being as good as with the use of electrical heating. It was necessary to keep the bath in a state of violent agitation, which was done by placing a high-speed stirrer below, and on the axis of, the heating coil.

The temperature of the vapor is indicated by a thermometer, *R*, placed with the bulb in the vapor exit. The liquid and packing temperature is read by means of the thermometer *S*. A third thermometer gives the temperature of the bath. These are calibrated, nitrogen-filled, 3-inch immersion thermometers. In normal operation the packing temperature and the vapor temperature were identical. The temperature of the bath was the same as that of the vapor, or, at a maximum, 0.5° F. above the temperature of the vapor.

To determine whether the apparatus functioned to produce equilibrium, it was fed with a solution of chloroform and toluene. The equilibrium diagram for this system at 744 mm. pressure is accurately known.[2]

The compositions of the condensed vapors and the residuums were found by determining the specific gravities and reading the compositions from a chart prepared by Geniesse.[3]

Each test run covered a 2-hour period, during which eight 15-minute vapor and residue samples were collected. The composition of each of these samples was determined, and also the compositions of the composites of the 15-minute samples. The results in a typical instance are shown in Table I. The composition of both vapor and residue was practically constant throughout the 2 hours, showing that the apparatus was giving uniform results when fed with a particular solution.

Table I—Composition of Successive Samples

Sample	Chloroform	
	Condensed vapor	Residual liquid
	Per cent by weight	
1	46.6	20.1
2	46.9	...
3	46.7	20.4
4	46.7	20.1
5	46.5	20.1
6	46.7	...
7	46.7	20.1
8	46.7	20.1
Composite	46.7	20.1

To ascertain the influence of feed rate the apparatus was fed with a solution of chloroform and toluene at rates from 6 to 15 cc. per minute. The results are shown in Table II. During the 6-hour period of this run, the temperature of the bath changed slightly, which accounts for the variation in composition of samples 4 and 5. From this and other similar experiments, the conclusion was reached that within the limits 6 to 15 cc. per minute the apparatus was such as to afford time for the establishment of equilibrium.

Table II—Effect of Rate of Feed on Composition of Products

Sample	Chloroform		Rate
	Vapor	Liquid	
	Per cent by weight		*Cc. per min.*
1	17.2	6.7	6
2	17.3	6.6	10.5
3	17.1	6.6	10.5
4	16.7	6.5	10.5
5	16.5	6.6	15

Since in running petroleum it would be necessary to operate for several hours in order to make samples large enough to be analyzed accurately, it was important to know the effect of slight variations in temperature on the composition of composite samples. Hence, a 2-hour run was made, feeding a solution of chloroform and toluene, and in which the temperature was gradually increased 0.5° F. and then brought back to the starting temperature. The results (Table III) show that the compositions of both vapor and residual liquid change gradually. The mean of the interval sample compositions agrees with compositions of the composite samples. The importance of accurate temperature control is indicated.

Several other runs were made in which chloroform and toluene were fed. The resultant data, together with those of Rosanoff, are presented as Figure 2. The agreement is excellent and justifies the conclusion that the apparatus was in fact producing equilibrium vapors and liquids. The following equation:

$$y = \frac{x}{0.320 + 0.517x + 0.163x^2}$$

developed by Geniesse to fit Rosanoff's data, can be used to extrapolate Rosanoff's data. The points determined in these experiments for liquid compositions of less than 0.25 chloroform fall on the extrapolated curve.

Table III—Variation in Composition of Vapor and Liquid with Small Change in Equilibrium Temperature

Sample	Chloroform	
	Vapor	Liquid
	Per cent by weight	
1	48.7	22.1
2	48.6	21.9
3	48.4	21.7
4	48.2	21.5
5	47.9	21.4
6	47.6	21.1
7	48.2	21.3
8	48.7	21.2
Average	48.3	21.5
Composite	48.4	21.5

Scope of the Work

The investigation included first the equilibrium single-flash vaporization of a paraffin-base petroleum at 250°, 300°, 350°, 400°, 450°, 500°, 550°, and 600°; and second, the equilibrium successive-flash vaporization of the same petroleum at 50° F. temperature intervals between 250° and 600° F. The procedure in making the single-flash experiments is self-evident. In making the successive-flash runs the crude was first flashed at 250° F.; the residuum obtained in this experiment was then flashed at 300° F., and so on to 600° F. In all experiments, yields of distillate were recorded and samples of the distillate and residuum were reserved for analysis. The feed rate in all runs was 10 cc. per minute, a rate at which equilibrium was established between the vapor and liquid phases. All yields were calculated on the basis of liquid volumes at 60° F.[4] Water at 32–34° F. was used for condensation of vapor and hence losses were small.

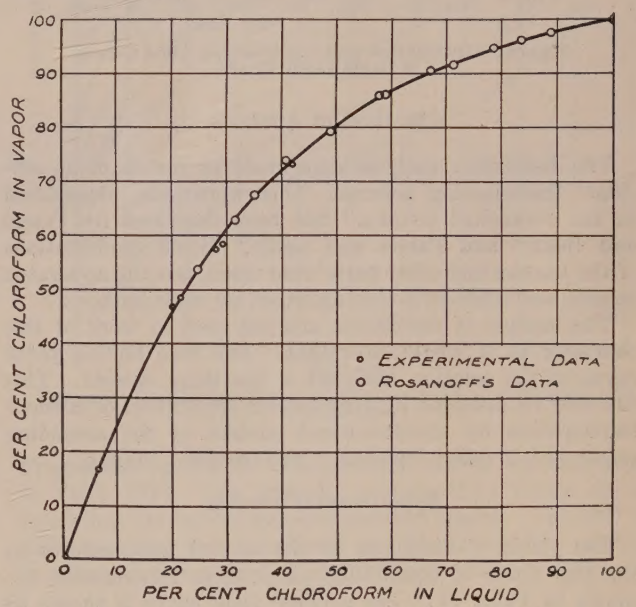

Figure 2—Chloroform-Toluene Equilibrium Data

The first single-flash series of runs was checked by a second series.* The results agreed so closely that the successive-flash runs were not duplicated.

[2] Rosanoff, *J. Am. Chem. Soc.*, **36**, 1803 (1914).

[3] Leslie and Geniesse, THIS JOURNAL, **18**, 591 (1926).

[4] *U. S. Bur. Standards Circ.* **154**, was used to make temperature corrections.

Crude Petroleum

The petroleum was a paraffin-base crude from Cabin Creek, W. Va., furnished through the courtesy of the Pure Oil Company. The specific gravity was 0.7947 at 60° F. The Standard Column and A. S. T. M. distillation curves are shown as curves 1 and 2 of Figure 3.

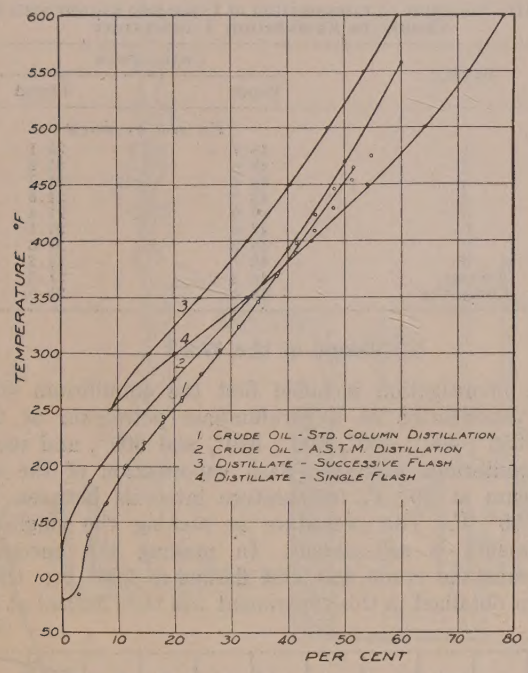
TEMPERATURE °F
PER CENT
1 CRUDE OIL - STD. COLUMN DISTILLATION
2 CRUDE OIL - A.S.T.M. DISTILLATION
3 DISTILLATE - SUCCESSIVE FLASH
4 DISTILLATE - SINGLE FLASH

Figure 3—Distillation and Vaporization Yield Curves of Cabin Creek Crude

Method of Analysis

The distillation analyses were made by means of an efficient fractionating column. This apparatus, designated as the "standard column," has been described by Peters and Baker[5] and Peters and Leslie.[6] Some modifications of the heaters and other parts were made, but the apparatus as used was essentially that described by these authors.

The method of distillation analysis used in work of this character is of great importance. The true boiling point curve of the solution analyzed is the thing desired. This can only be obtained by very careful application of efficient fractionation by countercurrent contact of the ascending vapor with a reflux liquid in a well-designed column.

Experimental Results

The yields of distillates at the several temperatures in the two series of equilibrium single-flash vaporization are shown in Table IV. The average yield curve is shown as curve 4 in Figure 3.

By flash temperature is meant the actual temperature at which vapor and liquid are separated and at which all the vapor and all the liquid are in equilibrium. In practice it is common to heat the liquid and then flash it upon pressure reduction. Operating in this way, the "flash temperature," as the term is here used, would be the temperature of liquid and vapor in the vaporizer, and not the temperature of the liquid in the heating coil. If no pressure is held on the heating coil, and vaporization consequently occurs in the coil, the temperature at the outlet end of the coil will be the same as, or close to, the equilibrium flash temperature.

[5] THIS JOURNAL, **18**, 69 (1926).
[6] *Oil Trade*, **17**, No. 3, 37 (1926).

In operating a laboratory heating and vaporizing system, control and feeding are difficult if pressure is held on the heating coil. For this reason the apparatus used in these experiments was operated at atmospheric pressure. No reliance was placed on the establishment of equilibrium in the heating coil, but the vaporizer, as already described, was so arranged as thoroughly to contact the liquid and vapor before they were separated.

The standard-column distillation curves of the distillates and residuums from the single-flash vaporizations are shown in Figure 4. The short curves in the upper part of the figure, and those to which dotted lines are extended, in the right-hand side, are A. S. T. M. distillation curves of the liquid remaining in the standard-column flask. A word of explanation with regard to this is necessary.

Table IV—Single-Flash Vaporization Yields

Flash Temperature	Yields of Distillate		
	Series A	Series B	Average
° F.	*Per cent*	*Per cent*	*Per cent*
250	8.4	8.6	8.5
300	19.94	19.96	19.95
350	32.51	33.09	32.80
400	43.5	45.00	44.22
450	54.05	54.07	54.06
500	64.22	63.92	64.07
550	71.61	72.42	72.01
600	78.28	78.12	78.20

The A. S. T. M. distillation curve of a crude petroleum, distillate, or residuum does not coincide with the true boiling point curve in the lower boiling end. However, the last 20 per cent of an A. S. T. M. curve is close to the true boiling point curve. In using the standard column apparatus it is not ordinarily convenient to obtain a curve for the last 20 per cent of a distillate. If a large sample were taken, it would be possible to obtain the curve to the 95 per cent point or beyond with the standard column. However, this greatly increases the time required for the work and is really unnecessary. Hence, the A. S. T. M. curves of the standard column flask residues were used, and a smooth curve dotted in connecting the standard column and A. S. T. M. curves.

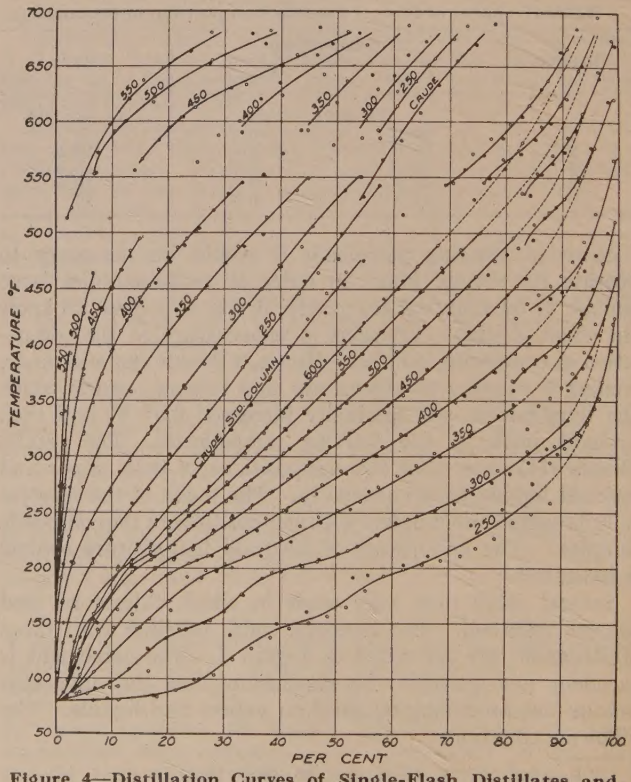

Figure 4—Distillation Curves of Single-Flash Distillates and Residuums

The procedure just outlined is satisfactory for the distillates but not for the residuums. The standard-column curves of the residuums could not be extended beyond the points shown because the temperature of the liquid in flask rose to 680° F., at which point cracking starts. The flask residues were then distilled in the A. S. T. M. apparatus, but this device is so poor a fractionating machine that the curves are displaced, as can be seen in Figure 4. These A. S. T. M. extensions do not constitute true boiling point curves and should not be so considered.

The results as depicted in Figure 4 are of considerable interest in themselves as well as in comparison with the successive-flash results presented below. Qualitatively, the most impressive thing is the fact that all vapors contain high-boiling compounds, and all residuums low-boiling compounds. The vapor flashed at 250° F. contains compounds boiling as high as 420° F. Probably it contains a small amount of still higher boiling material not detected because of the imperfection of the analysis. Likewise, the residuum from the flash at 550° F. contains compounds boiling as low as 170° F.

The futility of securing a high yield of gasoline of a given end point, and of producing a residuum free from low-boiling components by a process of simple separation of a vapor and liquid, is well illustrated. This is not a surprising result, for it would be expected that both the vapor and residuum formed from a solution such as petroleum would contain all components. The only question is—how much? Figure 4 gives the answer for the equilibrium single-flash vaporization of this type of crude.

Study of the curves of Figure 4 reveals several interesting regularities. For example, A. S. T. M. end points of the standard column flask residues bear a definite relationship to the flash temperatures. This is illustrated in Table V.

Table V—Relationship of Flash Temperature and Distillate End Point

Flash Temperature	End Point
° F.	*° F. above flash point*
250	173
300	161
350	161
400	167
450	170
500	172
550	161
Av.	165

Likewise, as shown in Table VI, a constant proportion of the distillate boils below the flash temperature. The 550° and 600° F. flash temperatures are not considered because the distillation curves at these temperatures were extrapolated.

Table VI—Relationship of Flash Temperature and Proportion of Distillate Boiling below Flash Temperature

Flash Temperature	Material in Distillate Boiling below Flash Temperature
° F.	*Per cent*
250	81.5
300	83.3
350	83.0
400	82.9
450	81.4
500	82.3
Av.	82.3

As the flash temperature is increased the percentage of material boiling under any particular temperature in the distillate decreases in a systematic manner. This is illustrated in Table VII.

Table VII—Progression Factors for Material Boiling below 300° F.

	Flash Temperature						
	300 °F.	350 °F.	400 °F.	450 °F.	500 °F.	550 °F.	600 °F.
Per cent below 300° F.	83.4	67.7	56.1	47.0	40.1	36.0	32.8
Difference	16.8	11.5	9.1	6.9	4.1	3.2	
Progression factor	0.73	0.79	0.76	0.59	0.78		

The progression factors for other temperatures are shown in Table VIII. As the flash temperature is raised more high-boiling material is included, with the result that the proportion of low-boiling material in the distillate is reduced. The regularity results from the fact that one is dealing with petroleum, a solution in which the distribution of components with temperature is uniform except in the low-boiling end.

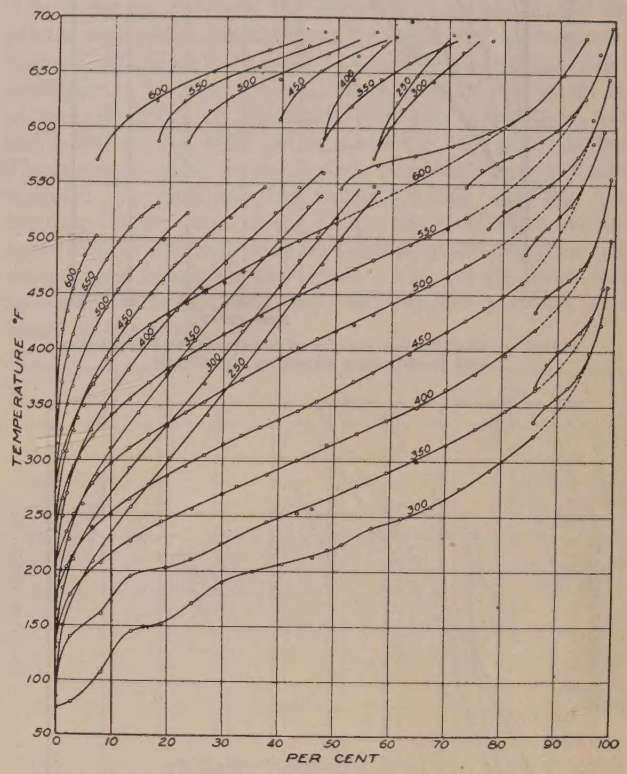

Figure 5—Distillation Curves of Successive Flash Distillates and Residuums

Progression factors for the residuum curves are also given in Table VIII. The intervals between these curves are so small that the factors appear somewhat erratic. The 250° F. residuum was not considered in calculating the average because the vapor formed at this temperature is abnormal.

Table VIII—Progression Factors

Distillate Curves		Residuum Curves	
Temperature on distillation curves	Progression factor	Temperature on distillation curves	Progression factor
° F.		*° F.*	
250	0.67	250	0.51
300	0.73	300	0.60
350	0.70	350	0.56
400	0.74	400	0.58
450	0.73	450	0.70
Av.	0.71	Av.	0.59

As the distillation curves of both distillates and residues are located with respect to each other in geometric progression, it is evident that by flashing alone a residuum can

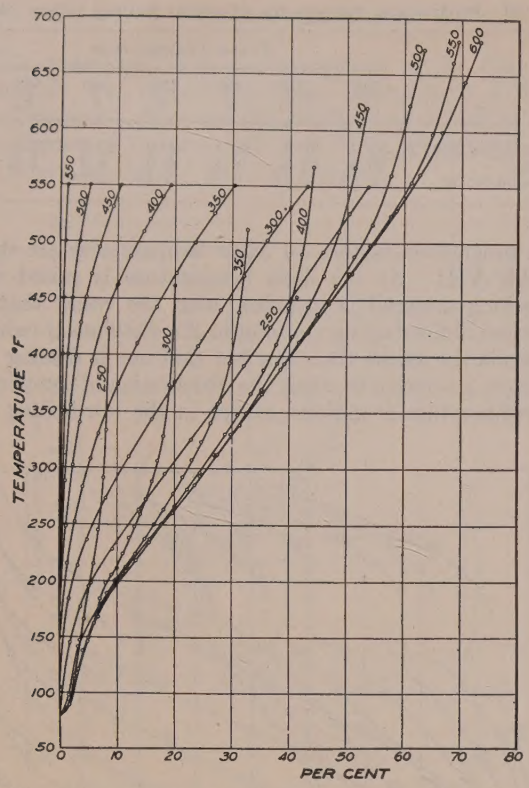

Figure 6—Distillation Curves of Single-Flash Distillates and Residuums Based on the Crude

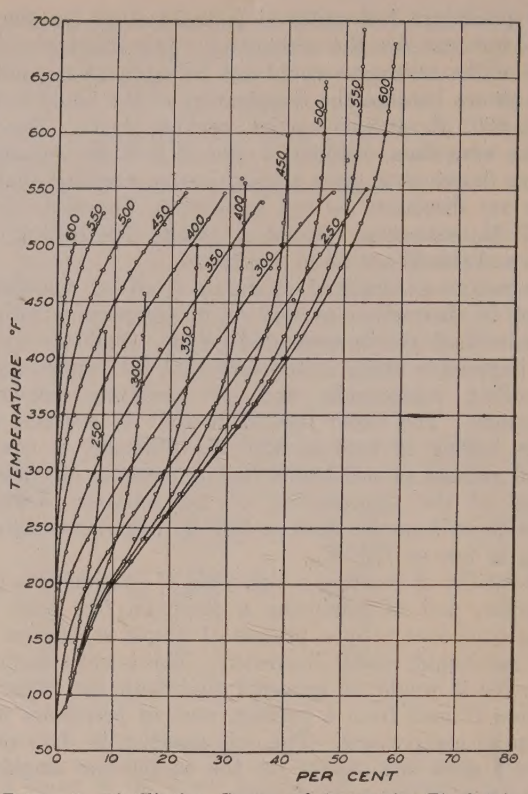

Figure 7—Distillation Curves of Successive-Flash Distillates and Residuums Based on the Crude

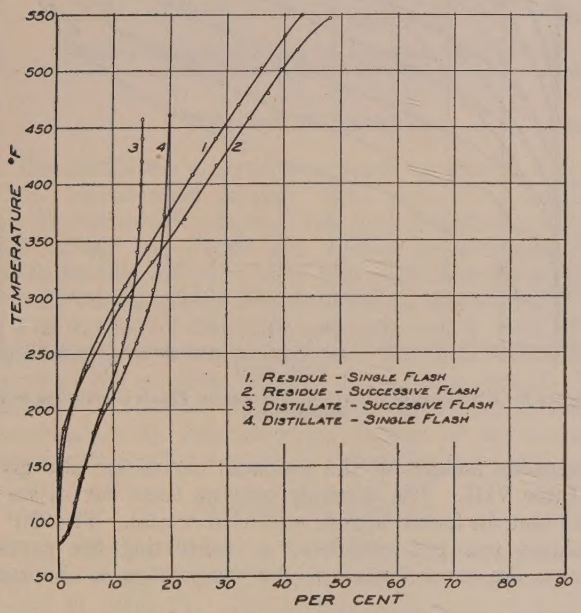
TEMPERATURE °F
PER CENT
1. Residue - Single Flash
2. Residue - Successive Flash
3. Distillate - Successive Flash
4. Distillate - Single Flash

Figure 8—Comparison of 300° F. Single and Successive Flashing Results

never be completely exhausted of its low-boiling components no matter what the flash temperature. The proportion of low-boiling components in the residuum becomes smaller and approaches zero as a limit as the flash temperature increases.

The prediction of distillation curves of distillates and residuums is possible if the progression factors are known. At least three distillation curves must be known in order to establish the progression factors.

The proportion of the residuums boiling below the flash temperature is approximately constant, as can be seen from Table IX.

Successive-Flash Vaporization

The industrial use of two or more flash vaporizations, as in pipe-still practice, or of vaporization in a series of stills operated continuously, makes it important to compare the results of such operations with equilibrium single flashing. The successive-flash vaporizations used in pipe-still practice are more effective in removing the low-boiling components than the succession of vaporizations from a series of stills. The vaporization in a continuously operated still is differential in character, and a differential vaporization is the least effective of any type. Differential vaporization is, in fact, the limiting process approached as the number of vapor increments is increased without limit. The results here presented show that vaporization in several increments is not so effective as single equilibrium flashing. Increasing the number of increments only makes the results worse.

Table IX—Proportion of Residuums Boiling below the Flash Temperature

Flash Temperature	Distillate in Residuums Boiling below Flash Temperature
° F.	*Per cent*
250	13.0
300	13.5
350	12.1
400	10.6
450	9.9
500	10.5
	Av. 11.6

The yields of distillates secured by successive equilibrium flashing at 50° F. intervals are shown in Table X. The cumulative percentages are shown as curve 3 in Figure 3. The contrast with curve 4 for single flashing is striking.

The standard-column distillation curves of the successive-flash distillates and residuums are shown as Figure 5. The residuum curves are directly comparable with the single-flash residuum curves. The distillate curves are not com-

parable, but must first be composited. The composited curves are described later.

Table X—Successive-Flash Vaporization Yields

Flash Temperature	Per Cent Vaporized				
	Based on charge		Based on crude		Cumulative—based on crude
	Distillate	Residuum	Distillate	Residuum	
° F.					
250	8.47		8.5	91.5	8.5
300	7.51	92.49	6.86	84.64	15.36
350	10.8	89.2	9.14	75.5	24.5
400	11.0	89.0	8.3	67.2	32.8
450	11.15	88.85	7.49	59.71	40.29
500	11.18	88.82	6.68	53.03	46.97
550	12.34	87.66	6.54	46.49	53.51
600	12.53	87.47	5.83	40.66	59.34

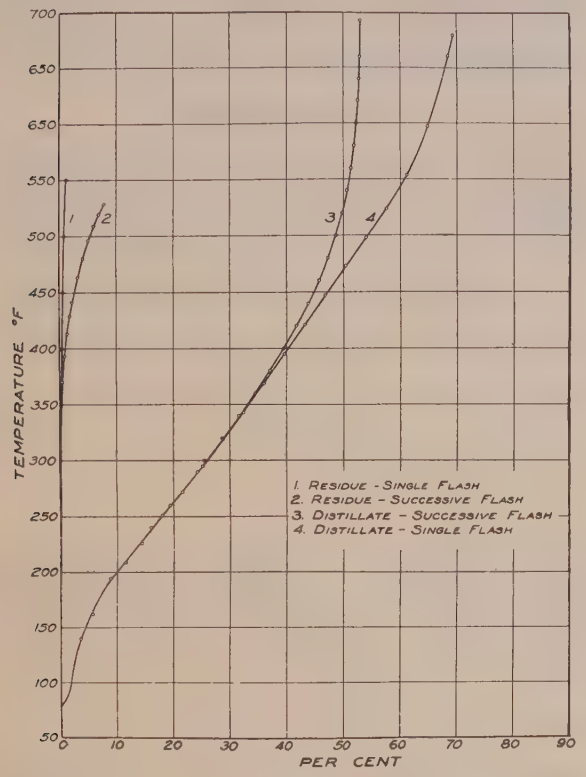
TEMPERATURE °F
PER CENT
1. Residue - Single Flash
2. Residue - Successive Flash
3. Distillate - Successive Flash
4. Distillate - Single Flash

Figure 9—Comparison of 550° F. Single and Successive Flashing Results

Consideration of the successive-flash curves shows several regularities. The A. S. T. M. end points of the standard-column flask residues of the distillates average 150° F. above the flash temperature. This is shown in Table XI.

Table XI—A. S. T. M. End Points of Standard Column Residues from Successive Flash Distillates

Flash Temperature	End Point
° F.	° F. *above flash point*
300	158
350	150
400	155
450	148
500	146
550	143
	Av. 150

The proportion of the successive-flash distillates boiling below the flash temperature is slightly smaller than in the case of the single-flash distillates, but is constant, as can be seen in Table XII. The proportion of components boiling below the flash temperature and contained in the successive-flash residuums is also shown in Table XII. The average is 16.4 per cent, as against 11.6 per cent for the single-flash vaporizations. This illustrates the superiority of single flashing from the standpoint of exhausting the residuums of low-boiling components.

Table XII—Proportion of Successive-Flash Distillates and Residuums Boiling below the Flash Temperature

Distillates		Residuums	
Flash temperature	Boiling below flash temperature	Flash temperature	Boiling below flash temperature
° F.	*Per cent*	° F.	*Per cent*
300	80.0	300	14.7
350	81.7	350	15.9
400	80.9	400	15.8
450	80.0	450	16.9
500	80.7	500	18.7
Av.	80.65	550	18.7
		Av.	16.4

Comparison of Results of Single and Successive Flashing

In order to compare the distillation curves of the distillates and residuums obtained by single and by successive flashing, all percentages must be based on the original crude petroleum. To base the single-flash data on the crude the percentage figures of the standard-column distillations were multiplied by the yield per cents of the materials distilled. The successive-flash residuum data were handled in the same manner. To calculate the successive-flash distillate percentages on the basis of the crude, the distillation percentages for each distillate were multiplied by the distillate yield percentages based on the crude. The results were then added to secure the cumulative temperature per cent curve based on the crude.

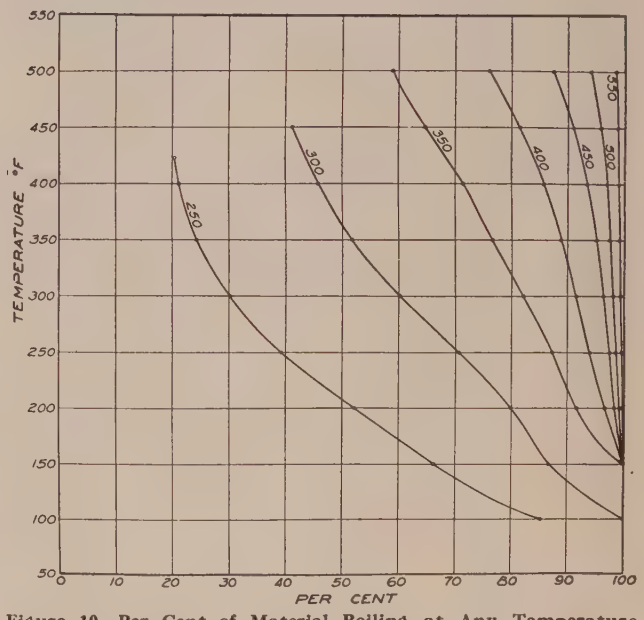

Figure 10—Per Cent of Material Boiling at Any Temperature Removed from the Crude by Single Flashing

The distillation curves of the single-flash distillates and residuums with percentages based on the crude are shown in Figure 6, and those for the successive-flash products in Figure 7. Comparison of corresponding curves of these figures shows both the higher yield of distillate secured by single flashing at any temperature and the boiling range of the substances included in the distillates and causing the higher yields.

Comparative curves can be plotted to display the differences in the results. Figures 8 and 9 present such curves for flashing at 300° F. and at 550° F., respectively. Based on the crude, the single-flash residuums contain less low-boiling material than the successive flash residuums, and

the single-flash distillates more material boiling at any point than the successive-flash distillates. This is true of the upper part of the curves. At lower temperatures the curves

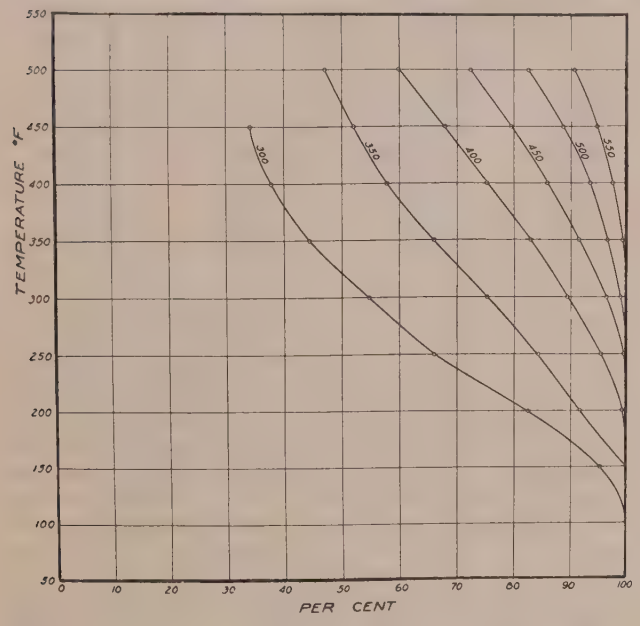

Figure 11—Per Cent of Material Boiling at Any Temperature Removed from the Crude by Successive Flashing

coincide, showing that both processes of vaporization exhausted the residuum of its lowest boiling components. However, even when flashing at 550° F. the successive-flash residuum contains 2.8 per cent (based on the crude) of distillate boiling below 450° F. This is entirely too much gasoline to neglect in practice. If any form of successive vapor formation is used, the residue must be exhausted in a stripping column if high yields of gasoline are to be obtained.

To show the difference in the distribution of components in the single and successive flash distillates, the curves of Figures 6 and 7 may be graphically differentiated. For brevity the derived curves are omitted here, but attention is called to this procedure in studying distillation data.

The per cent of material, boiling at any temperature and contained in the crude, removed by the two processes of vaporization at the several temperatures is shown in Figures 10 and 11. The larger total distillate yields, or the greater percentage removal of particular components, secured by single flashing can be readily explained. When all the vapor is removed in one portion the lower boiling components exert what may be regarded as a "steam distillation effect" with respect to the higher boiling components. It is as if the higher boiling components were distilled under partial vacuum at the particular temperature. This effect is obviously operative to a less degree in successive flashing.

Heat Requirement for Vapor Formation

The data presented show single-flash vaporization to be superior to successive flashing with regard to yield and composition of vapor. In practice, the total heat required is also important. Consequently, the results should be compared on a heat basis. In making these calculations the specific heat data of Eckhart[7] and the latent heat data of Leslie, Geniesse, Legatski, and Jagrowski[8] were used.

The heat required to remove any given per cent of vapor from one gallon of the crude petroleum is shown in Figure 12.

[7] *Mech. Eng.*, **47**, 539 (1925).

[8] THIS JOURNAL, **18**, 45 (1926).

The superiority of single flashing is clearly indicated. Not only is less heat required, but the temperature to which the oil must be heated to remove a given percentage is lower and hence somewhat more favorable to the process of heat transfer. Furthermore, a difference of 50° to 75° F. at a temperature of 550° to 600° F. may easily mean the difference between coking and not coking the heating surfaces of an apparatus. Thermal decomposition of an oil occurs in the superheated film next the heating surfaces. At 680° F. temperature in the body of the oil, the portion of the oil in the superheated film is at a temperature sufficiently higher to cause rapid cracking and hence coking. The temperature of the oil in the superheated film is a function of the rate of heat flow as well as of the bulk oil temperature. Hence, if vaporization can be effected at 500° to 550° F. rather than 600° to 650° F., not only can coking be avoided, but the rate of heat transfer and capacity of the apparatus can be materially increased.

Practical Application

The ideal method of vapor formation for most purposes is the one that economically exhausts the residuum of gasoline and results in a vapor of such composition as to be easily fractionated to produce gasoline, kerosene, and gas oil.

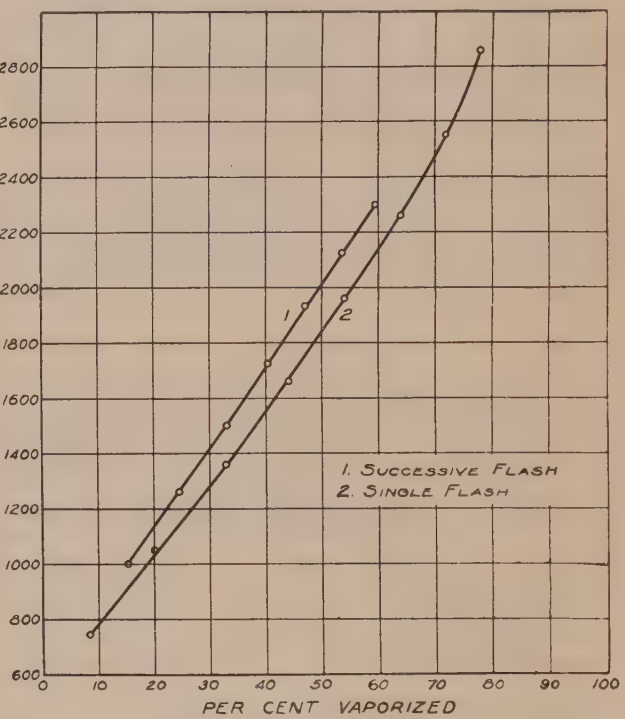

Figure 12—Heat Required to Remove Any Per Cent of Distillate from One Gallon of Crude

The data presented above show single-flash vaporization to be superior to successive flashing. Worst of all is differential vaporization or batch distillation, the limiting process of successive flashing. Yet, in practice, batch distillation is still used by many of the largest refiners. Also still batteries, operated continuously, and representative of differential incremental vaporization, are widely used as a preferred type of equipment.

The results presented here suggest that refinery practice as regards vapor formation should receive serious consideration. The single equilibrium flash is easily possible and is, in fact, common in pipe-still practice. Also shell stills can be, and are, operated as single continuous units. These procedures are to be recommended.